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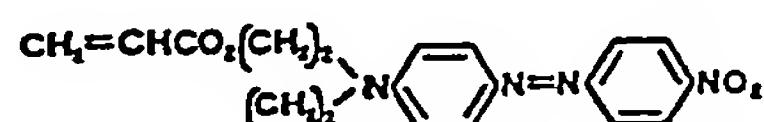
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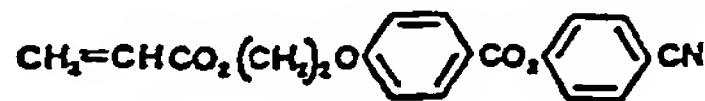
(54) Electro optic liquid crystal polymers

(57) A method of processing electro optic liquid crystal polymers comprises applying a high DC poling field to the polymer at a temperature below Tg such that liquid crystal properties are exhibiting despite a nominal isotropic nature of the polymer. The polymer comprises a polymeric backbone having side groups with non linear electro optic properties and side groups with liquid crystal properties, and can be made from combinations of the illustrated monomers A/2ANAS, A/20CPB, A/20CBB, A/20CBAB and A/60MBB.

A/2ANAS



A/20CPB



A/20CBB



A/20CBAB



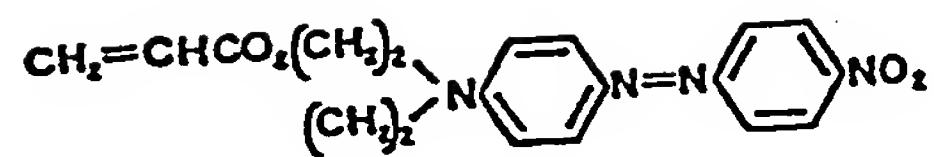
A/60MBB



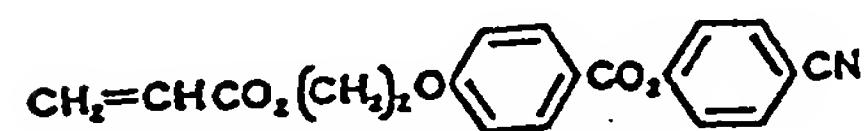
Figure 1 Chemical structure of the monomers

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A/2ANAS



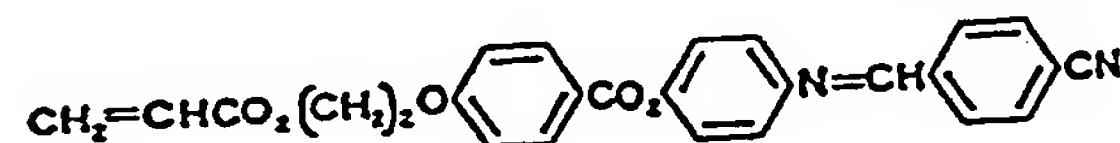
A/20CPB



A/20CBB



A/20CBAB



A/60MBB



Figure 1 Chemical structure of the monomers

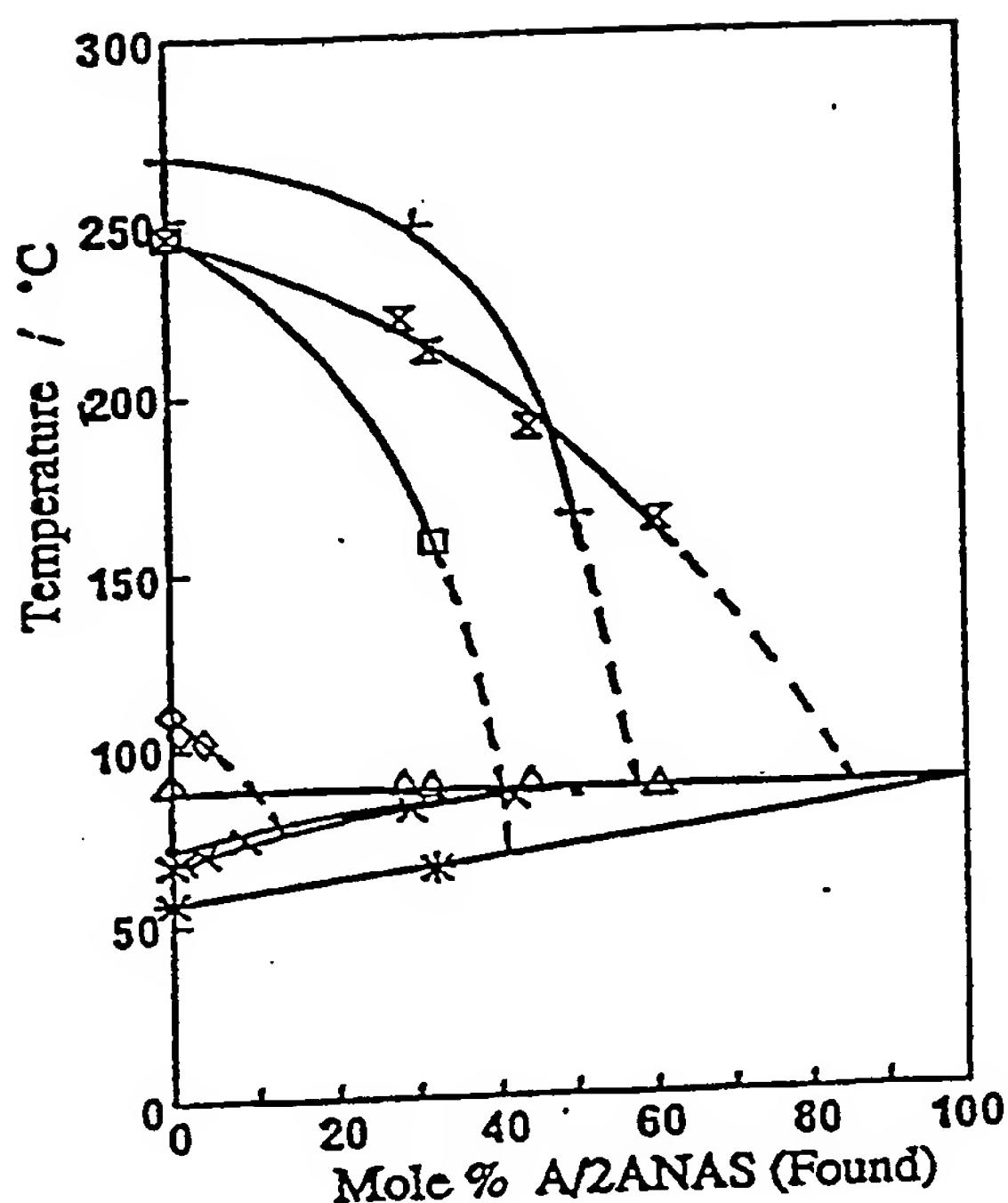


Figure 2 Phase diagram for the NLO liquid crystal copolymers. Symbols; T_g , A/2OCBAB (●), A/6OMBB (□), A/2OCPB (×), A/2OCB (◇); T_{NI} , A/2OCBAB (+), A/6OMBB (△), A/2OCPB (◊), A/2OCB (✗).

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Detailed description: This is a line graph with 'Time / Days' on the x-axis (ranging from 0 to 240) and '% Initial remanent Value' on the y-axis (ranging from 50 to 110). There are four data series: 1) 3.5 M% Crystallized at 49°C (solid squares), showing a slow decrease from ~100% to ~95% over 240 days. 2) 3.5 M% Liquid Crystallized at 65°C (asterisks), showing a rapid initial drop to ~85% by day 10, followed by a plateau. 3) 30 M% Crystallized at 77°C (open squares), showing a steady linear decrease from ~100% to ~55% over 240 days. 4) 30 M% Liquid Crystallized at 88°C (open diamonds), showing a very rapid initial drop to ~80% by day 10, followed by a plateau.

Time / Days	% Initial remanent Value (49°C)	% Initial remanent Value (65°C)	% Initial remanent Value (77°C)	% Initial remanent Value (88°C)
0	100	100	100	100
10	99	85	98	80
20	98	84	96	78
40	97	83	94	76
60	96	82	92	74
80	95	81	90	72
100	94	80	88	70
120	93	79	86	68
140	92	78	84	66
160	91	77	82	64
180	90	76	80	62
200	89	75	78	60
220	88	74	76	58
240	87	73	74	56

Figure 3 Electro-optic measurements on 30 Mole% A/2ANAS in A/2OCPB as a function of poling field when poling at 20°C (●) and 10°C (▲) below T_g .

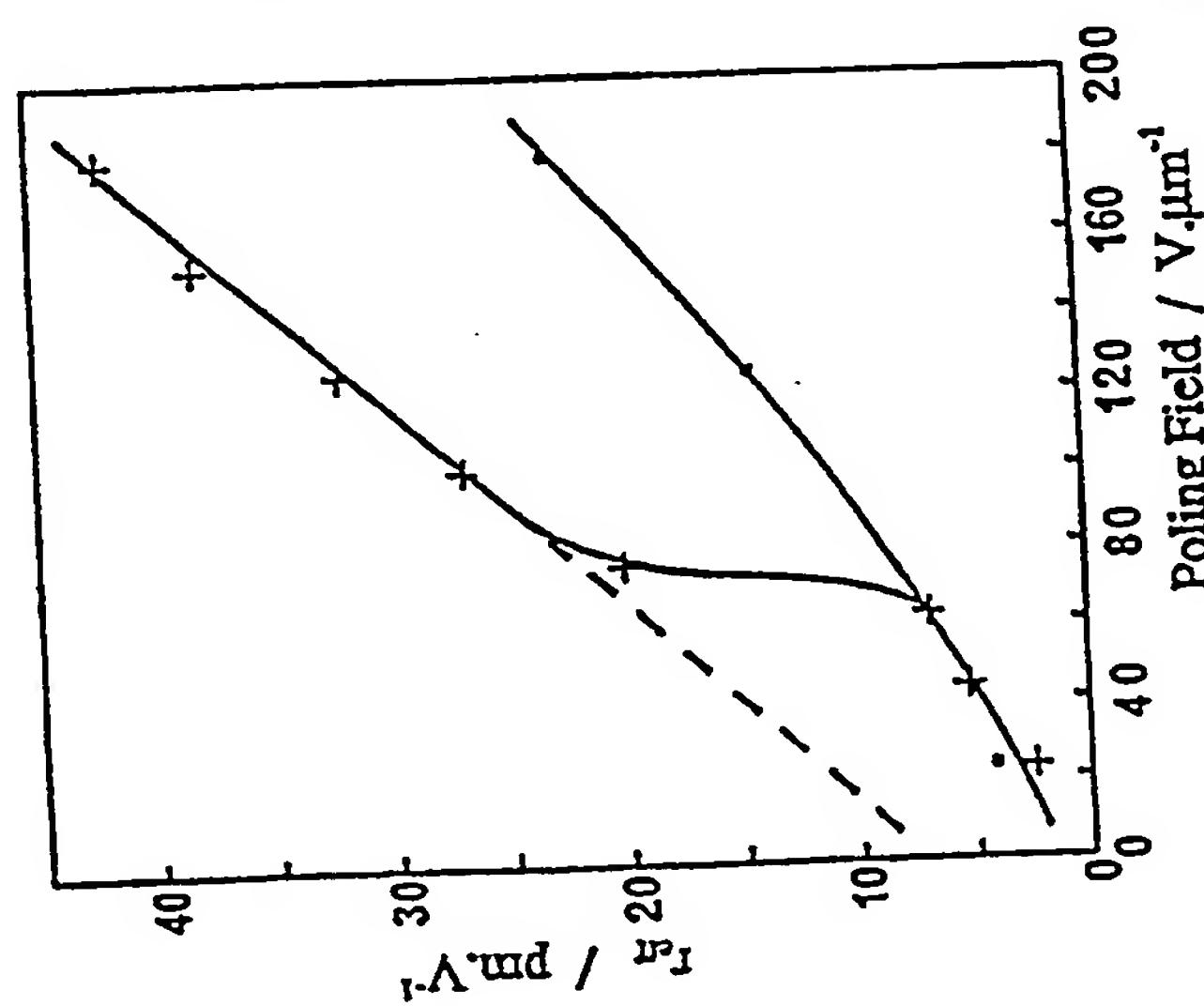


Figure 4 Thermal stability of a range of copolymers of A/2ANAS and A/2OCPB stored at different temperatures below T_g : 3.5 M% Liquid Crystallized at 49°C (■), 65°C (★) and 88°C (△) below T_g ; 30 M% Liquid Crystallized at 77°C (□) and 61°C (○) below T_g

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ELECTRO OPTIC LIQUID CRYSTAL POLYMERS

The present application relates to electro optic liquid crystal polymers and to a method of producing and processing such polymers.

It has been previously proposed to provide polymers comprising a polymeric backbone having side chains with non linear electro optic properties and side chains with liquid crystal properties. In order to obtain a non centrosymmetric arrangement for the molecules to display second order optical effects, the polymer is processed by heating to a temperature above the glass transition temperature (T_g) of the polymer followed by applying a D.C. poling field and subsequently cooling the polymer to below T_g while maintaining the poling field and thus freezing in the non centrosymmetric structure.

Throughout this document, the term "electro optic liquid crystal polymer" will be used to indicate a molecule having a polymeric backbone and side chains having non linear electro optical properties and side chains having liquid crystal properties, unless otherwise indicated.

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In accordance with one aspect of the present invention, there is provided an electro optic liquid crystal polymer which is isotropic whilst processing, but will exhibit liquid crystal properties after poling in high D.C. fields at temperatures at or below Tg of the polymer.

In accordance with a further aspect of the invention, there is provided a method of producing electro optic liquid crystal polymers as defined above comprising copolymerising a monomer having a polymerisable group and a non linear electro optic group with a monomer comprising a polymerisable group with a liquid crystal group.

In accordance with a still further aspect of the invention, there is provided a method of processing an electro optic liquid crystal polymer comprising applying a high poling field to the isotropic polymer at a temperature at or below Tg such that it exhibits hC properties.

The D.C. poling is typically carried out within 20°C of Tg and the poling field is preferably high, eg. greater than 50 volts/micron and were typically more then 100 V/micron.

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The present invention will now be described, by way of example, with reference to the following preparation examples and to the accompanying drawings in which:-

Figure 1 shows chemical structure of the monomers used to produce the polymers,

Figure 2 shows the phase diagram for the prepared copolymers,

Figure 3 shows electro optic measurements of a copolymer, and

Figure 4 shows the thermal stability of a range of copolymers.

The monomers used in the preparation are examples of polymers according to one aspect of the invention as shown in figure 1 and different proportions of the monomers were used where appropriate. The monomer A/2ANAS is an acrylate ester of Disperse Red 1 which is a readily obtainable material possessing high quadratic hyperpolarisability. The copolymerisations were carried out using ABIN initiated polymerisation in dry dimethylsulphoxide at 85°C for 40 hours in a nitrogen atmosphere. Repeated precipitation from

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methanol gave copolymers which were found to be free of monomers by TLC and GPC.

Analysis of copolymers showed molecular weights generally in the region of about 4000 for each material as measured by GPC, indicating that about 10 acrylate units were present in each copolymer chain. The polymerisation yield ranged from about 65% when 1-2 Mol% of A/2ANAS was included to about 5% when 50 Mol% of A/2ANAS was included.

The phased transition temperatures of the copolymers were determined using optical microscopy and differential scanning calorimetry. Figure 2 shows the phase diagram of various copolymers including A/2ANAS.

Cells were prepared which include the copolymers indicated above using a thermal compression technique. A small amount of de-gassed polymer was placed on an ITO coated glass substrate. A similar glass substrate was placed on top of the polymer and the sandwich was heated to a temperature above T_g of the polymer and compressed in a controlled way such that a flat cell was formed. To achieve D.C. poling the cells were heated at a rate of $10^{\circ}\text{C}/\text{minute}$ to a temperature just below T_g and a poling field of up to 180 volts per micron was applied for 10 minutes. After this

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time, the sample was rapidly cooled to room temperature and the field removed.

Figure 3 shows electro optic measurements on an electro optic copolymer according to the invention, the measurements being taken at 20°C and 10°C below Tg for that copolymer. The increase in r_{eff} for 10°C below Tg shows that liquid crystal ordering is taking place in what is nominally an isotropic copolymer which would not be expected to show liquid crystal behaviour. Similar behaviour may be observed with other copolymers.

Figure 4 shows the thermal stability of a range of copolymers when stored at temperatures below Tg. This thermal stability is measured by measuring the electro optical properties and as will be apparent, polymers exhibiting liquid crystal properties demonstrate greater thermal stability than isotropic polymers.

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CLAIMS

1. An electro optic liquid crystal polymer comprising a polymeric backbone having side groups with non linear electro optic properties and side groups with liquid crystal properties, said polymer being isotropic but after poling in a high DC field at temperatures at or below the glass transition temperature exhibiting liquid crystal properties.
2. The method of processing an electro optic liquid crystal comprising forming an electro optical liquid crystal polymer and applying a high poling field to said polymer while maintaining a temperature below Tg.
3. A method as claimed in claim 2 wherein the poling takes place at within 20°C of Tg.
4. A method as claimed in claims 2 or 3 where the poling field is greater than 50 volts/micron.
5. A method as claimed in claim 4 wherein the poling field is greater than 100 V/micron.
6. A method of forming an electro optic liquid crystal

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polymer as claimed in claim 1 comprising copolymerising a monomer having a polymerisable group and a non linear electro optic group with a monomer having a polymerisable group and a liquid crystal group.

7. a copolymer of A/2ANAS and A/20CPB.

8. A copolymer as claimed in claim 7 comprising up to 42 M% A/2ANAS.

9. A copolymer as claimed in claim 8 comprising up to 30% A/2ANAS.

10. A copolymer as claimed in claim 9 comprising up to 10 M% A/2ANAS.

11. A method of processing an electro optical liquid crystal polymer which is substantially as herein described.

12. An electro optic liquid crystal polymer which is substantially as herein described.

13. A method of forming an electro optic liquid crystal polymer which is substantially as herein described.